

SRI International

Annual Report • January 1997

CHARACTERIZATION OF HYDROGEN INGRESS IN HIGH-STRENGTH ALLOYS

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SRI Project PYU-7495

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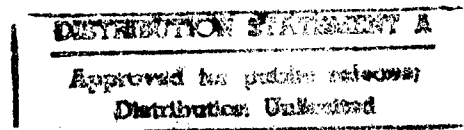
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Contract No. N00014-95-C-0313

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19970130 014

DTIC QUALITY INSPECTED 3

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE Jan 97	3. REPORT TYPE AND DATES COVERED Annual 20 Sept 95-19 Sept 96		
4. TITLE AND SUBTITLE Characterization of Hydrogen Ingress in High-Strength Alloys		5. FUNDING NUMBERS N00014-95-C-0313		
6. AUTHOR(S) Bruce G. Pound				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) SRI International 333 Ravenswood Ave. Menlo Park, CA 94025		8. PERFORMING ORGANIZATION REPORT NUMBER PYU-7495		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research, ONR 332 800 N. Quincy St. Arlington, VA 22217-5000		10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release - distribution unlimited		12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) The effect of heat treatment on irreversible hydrogen (H) trapping was investigated for Alloy K-500 [UNS N05500], with the goal of providing a more detailed insight into the factors governing the intrinsic susceptibility to hydrogen embrittlement (HE). A potentiostatic pulse technique was used to determine irreversible trapping constants (k) and H entry fluxes for annealed and annealed-aged (AA) specimens of cold drawn Alloy K-500 that had been used earlier to provide as-received (unannealed, cold drawn) and direct aged (DA) specimens. The alloy was tested in four conditions: annealed for 0.5 h, annealed for 0.5 h and aged for 8 h, annealed for 0.5 h and aged for 16 h, and annealed for 0.25 h and aged for 8 h. The type of heat treatment can produce marked differences in irreversible trapping. The key factor was the annealing step rather than the aging time. The intrinsic susceptibility to HE, as defined by k, is increased considerably by annealing, whereas aging has a negligible effect for the annealed alloy and only a modest effect for the unannealed alloy. The intrinsic susceptibilities for the AA and DA alloys can be correlated with the observed resistances to HE, implying that the decrease in the resistance to HE produced by annealing is caused to a large extent, if not entirely, by a change in the number or the type of irreversible traps.				
14. SUBJECT TERMS Alloy K-500, Heat Treatment, Potentiostatic Pulse, Hydrogen Trapping, Trapping Model, Hydrogen Ingress, Hydrogen Embrittlement		15. NUMBER OF PAGES 17		
		16. PRICE CODE		
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

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PREFACE

This annual report describes work performed under Office of Naval Research (ONR) Contract No. N00014-91-C-0263 in a continuation of our program to investigate hydrogen ingress into various high-strength alloys, particularly in terms of irreversible trapping, with a view to characterizing the susceptibility of the alloys to hydrogen embrittlement (HE). A technique referred to as hydrogen ingress analysis by potentiostatic pulsing (HIAPP) was used to obtain anodic current transients for the alloys in 1 mol L⁻¹ acetic acid/1 mol L⁻¹ sodium acetate, and the transients were analyzed using a diffusion/trapping model under interface control conditions to evaluate the trapping constant and hydrogen entry flux in each case.

The report is presented as an Executive Summary followed by a paper that will be submitted for publication in the journal *Corrosion*. The paper is titled "The Relationship Between Heat Treatment and Hydrogen Trapping in Alloy K-500" and examines the effects of annealing and of aging time on the irreversible trapping characteristics of alloy K-500.

EXECUTIVE SUMMARY

High performance alloys often must possess a combination of properties such as strength, toughness, and corrosion resistance. However, their resistance to hydrogen embrittlement (HE) remains a concern in many situations. Microstructural defects in these and other alloys provide potential trapping sites for hydrogen and so can play a crucial role in determining an alloy's intrinsic susceptibility to HE. However, whether embrittlement will actually occur is also affected by other factors, including the amount of hydrogen entering the alloy. Consequently, alloys need to be characterized in terms of both trapping capability and the rate of hydrogen entry to assess their likelihood of embrittlement.

This report describes work performed during a continuation of our program with the Office of Naval Research (ONR) to investigate hydrogen ingress in various alloys, particularly in terms of irreversible trapping, with a view to characterizing the susceptibility of the alloys to HE. A technique referred to as hydrogen ingress analysis by potentiostatic pulsing (HIAPP) was used to obtain anodic current transients for the alloys in 1 mol L⁻¹ acetic acid/1 mol L⁻¹ sodium acetate containing 15 ppm As₂O₃. The transients were analyzed using a diffusion/trapping model under interface control conditions to evaluate the apparent trapping constant (k_a) and hydrogen entry flux in each case. Where possible, k_a was then used to determine the irreversible trapping constant (k) and the density of irreversible traps.

The study involved alloy K-500 in four conditions: annealed for 0.5 h, annealed for 0.5 h and aged for 8 h, annealed for 0.5 h and aged for 16 h, and annealed for 0.25 h and aged for 8 h. The values of k were compared with those for direct aged (DA) alloy K-500 and two annealed and aged (AA) heats of alloy K-500 that had been studied previously. The type of heat treatment can produce marked differences in irreversible trapping. The key factor was the annealing step rather than the aging time. The intrinsic susceptibility to HE, as defined by k , is increased considerably by annealing, whereas aging has a negligible effect for the annealed alloy and only a modest effect for the unannealed alloy. The intrinsic susceptibilities for the AA and DA alloys can be correlated with the observed resistances to HE, implying that the decrease in the resistance to HE produced by annealing is caused to a large extent, if not entirely, by a change in the number or the type of irreversible traps.

The Relationship Between Heat Treatment and Hydrogen Trapping in Alloy K-500*

ABSTRACT

The effect of heat treatment on irreversible hydrogen (H) trapping was investigated for Alloy K-500 [UNS N05500], with the goal of providing a more detailed insight into the factors governing the intrinsic susceptibility to hydrogen embrittlement (HE). A potentiostatic pulse technique was used to determine irreversible trapping constants (k) and H entry fluxes for annealed and annealed-aged (AA) specimens of cold drawn Alloy K-500 that had been used earlier to provide as-received (unannealed, cold drawn) and direct aged (DA) specimens. The alloy was tested in four conditions: annealed for 0.5 h, annealed for 0.5 h and aged for 8 h, annealed for 0.5 h and aged for 16 h, and annealed for 0.25 h and aged for 8 h. The type of heat treatment can produce marked differences in irreversible trapping. The key factor was the annealing step rather than the aging time. The intrinsic susceptibility to HE, as defined by k , is increased considerably by annealing, whereas aging has a negligible effect for the annealed alloy and only a modest effect for the unannealed alloy. The intrinsic susceptibilities for the AA and DA alloys can be correlated with the observed resistances to HE, implying that the decrease in the resistance to HE produced by annealing is caused to a large extent, if not entirely, by a change in the number or the type of irreversible traps.

INTRODUCTION

Alloy K-500 is known to be susceptible to hydrogen embrittlement (HE), but its susceptibility is influenced considerably by the type of heat treatment. Tests on cold worked Alloy K-500 have shown that the ultimate tensile strength of annealed and aged (AA) specimens which were cathodically precharged for 16 days decreased by 35%, whereas the strength of the direct aged (DA) alloy actually increased slightly.¹

In recent work at SRI International, the type of heat treatment was also found to have a marked effect on the irreversible trapping of hydrogen (H) in Alloy K-500.² A potentiostatic pulse technique was used to determine the rate constants for irreversible trapping (k) for alloy K-500 in the cold drawn and DA condition (yield strength of 1096 MPa) and the AA condition (yield strength of ~700 MPa). k was found to be more than twice as large for the AA alloy as it was for the DA alloy. The order of the k values for the two types of aged Alloy K-500 correlated with their

* To be submitted to *Corrosion*.

observed resistance to HE, based on the tensile strength tests. Thus, the effect of heat treatment on the HE resistance of alloy K-500 appeared to result at least partly from changes in the irreversible H traps.

The main differences in heat treatment between the DA and AA alloy were the annealing step and the aging time (16 h for AA compared with 8 h for DA). In the case of Ni 200 (≤ 0.15 C), prolonged exposure between 425° and 650°C can cause graphite precipitation,³ which has been found to occur at grain boundaries in Ni 200 aged for 24 h at 450° to 650°C.⁴ Thus, aging time may have been a key difference between the DA and AA Alloy K-500 with respect to graphite precipitation. However, annealing may play the crucial role. AA specimens with different annealing times exhibited different levels of grain boundary C, which implies that annealing renders the alloy more prone to graphite precipitation during aging. Thus, it is unclear whether the higher k for the AA alloy resulted from the longer aging time or from inclusion of the annealing step. In fact, it is not even certain that either aging time or annealing have such a pronounced effect on the irreversible trapping characteristics of Alloy K-500.

In the present work, the potentiostatic pulse technique was used to examine irreversible trapping in Alloy K-500 as a function of heat treatment to determine whether aging time or annealing is responsible for irreversible trapping differences observed between the AA and DA alloys. Values of k were obtained for annealed and AA specimens of the cold drawn Alloy K-500 that had been used earlier to provide as-received (unannealed, cold drawn) and DA specimens. These values were compared with results for the alloy in the unannealed and the DA conditions as well as for the earlier AA specimens, which were obtained elsewhere.[†] The results were intended to elucidate whether heat treatment is a critical factor in Alloy K-500's resistance to HE and, if so, which is the key aspect of the heat treatment.

EXPERIMENTAL PROCEDURE

Table 1 gives the compositions of the cold drawn Alloy K-500 and the AA alloy (in two heats, denoted as AA-1 and AA-2) used previously. AA-1 and AA-2 were supplied as sections of bar that had been solution-annealed and aged at 607°C for 16 h to give a yield strength in the range 689-724 MPa. The alloys had a similar bulk composition, but the AA-2 alloy exhibited a moderate amount (~20%) of graphitic C at the grain boundaries, whereas the AA-1 alloy contained only a small amount (1-3%) of grain boundary C.^{5,6}

The cold drawn (CD) alloy was supplied as 1.27-cm-diameter rod, which was direct aged in the previous work to give a yield strength of about 1096 MPa. The direct aging treatment

[†] Provided by Dr. M. Natishan, formerly at the David Taylor Research Center, Department of the Navy, and now at the University of Maryland.

followed the procedure recommended for CD rods ≤ 3.8 cm in diameter: Heat at 600°C for 8 h and then cool to 480°C at a rate of 11°C/h.² In the present work, the CD alloy was annealed at 982°C and, where relevant, aged at 600°C. The alloy was tested in four conditions: (1) annealed for 0.5 h, (2) annealed for 0.5 h and aged for 8 h, (3) annealed for 0.5 h and aged for 16 h, and (4) annealed for 0.25 h and aged for 8 h. These conditions are denoted as 0.5h-A, 0.5h-AA, 0.5h-AA-16h, and 0.25h-AA, respectively. During aging, particles of Ni₃(Ti,Al) are precipitated throughout the matrix of Alloy K-500.⁷

Details of the electrochemical cell and instrumentation were given previously.⁸ The test electrodes of Alloy K-500 consisted of a 1.27-cm length of rod (as-supplied or machined) press-fitted into a polytetrafluoroethylene sheath so that only the planar end surface was exposed to the electrolyte. The surface was polished before each experiment with SiC paper and then 0.05- μ m alumina powder. The electrolyte contained 1 mol L⁻¹ acetic acid (CH₃COOH) and 1 mol L⁻¹ sodium acetate (CH₃COONa) with 15 ppm As₂O₃ and was deaerated continuously with Ar before and throughout data acquisition. The potentials were measured with respect to a saturated calomel electrode (SCE). All tests were performed at 22 \pm 1°C.

The test electrode was cathodically charged with H at a constant potential E_c for a time t_c , after which the potential was stepped in the positive direction to a value 10 mV negative of the open-circuit potential E_{oc} . Anodic current transients were obtained over a range of charging times, typically from 5 to 60 s, at different overpotentials ($\eta = E_c - E_{oc}$). The open-circuit potential of the test electrode was measured immediately before each charging time and was also used to monitor the stability of the alloy surface.

ANALYSIS

The current transients were analyzed using a diffusion/trapping model based on a constant entry flux of H at the surface.^{8,9} According to the model, the total anodic charge ($C\ m^{-2}$) is given by

$$q'(\infty) = FJt_c \{ 1 - e^{-R/(\pi R)^{1/2}} - [1 - 1/(2R)]\text{erf}(R^{1/2}) \} \quad (1)$$

where F is the Faraday constant, J is the ingress flux in $\text{mol}\ m^{-2}\ s^{-1}$, and $R = k_a t_c$. The charge $q'(\infty)$ is equated to the charge (q_a) passed during the experimental anodic transients. q_a can be associated entirely with absorbed H, since the adsorbed charge is almost invariably negligible. k_a is an apparent rate constant for irreversible trapping measured in the presence of reversible traps. It

is related to the irreversible trapping constant (k) by kD_a/D_L , where D_a is the apparent diffusivity and D_L is the lattice diffusivity of H.

k_a and therefore k are related to the density (N_i) and radius (d) of particles or defects providing irreversible traps by Equation (2):

$$N_i = k_a a / (4\pi d^2 D_a) \quad (2)$$

where a is the diameter of the metal atom.^{10,11} The value of a for an alloy is taken as the mean of the atomic diameters weighted in accordance with the atomic fraction of each element. The trap radius is estimated from the dimensions of heterogeneities that are potential irreversible traps, and trap densities are then calculated for the different values of d . In this way, the principal irreversible trap can be identified by comparing the values of N_i with the actual concentrations of specific heterogeneities.

k has been used in our previous work as an index for characterizing an alloy's intrinsic susceptibility to HE.^{12,13} The correlation between k and the observed resistance to HE suggests that k contains enough key parameters to be effective as an index of susceptibility for the alloys studied at their respective yield strengths.

RESULTS

For the constant flux model to be applicable, it must be possible to determine a trapping constant for which J is independent of charging time. Equation (1) could in fact be fitted to the experimental data for q_a to obtain values of k_a and J that satisfy this requirement at each potential. Values of k_a and J for duplicate tests on Alloy K-500 in each condition are given in Table 2. In all cases, k_a is independent of charging potential. Table 3 shows the overall mean value of k_a for each condition. The values of k_a for all conditions, except 0.25h-AA, were the same within experimental uncertainty. In the case of the 0.25h-AA alloy, k_a was lower than those for the 0.5-h annealed alloys but higher than that for the DA alloy, which had not been annealed at all before aging.

The hydrogen flux for each condition was constant over the range of charging times for each overpotential and generally increased to some extent with overpotential. The increase was to be expected because of the dependence of J on the surface coverage of adsorbed H. The flux did not show a significant difference between the four heat treatments.

DISCUSSION

Irreversible Trapping Constants

The irreversible trapping constants (k) were derived from k_a by using diffusivity data for the "pure" alloy to obtain the lattice diffusivity (D_L) and for the actual alloy to obtain the apparent diffusivity (D_a), so that the effect of reversible traps could be taken into account. From the viewpoint of diffusivity, the "pure" Alloy K-500 can be taken as 65Ni-35Cu. Minor elements (either in their atomic form or as intermetallics precipitated during aging) in the actual alloys were treated as reversible traps and in fact were assumed to be primarily responsible for reversible trapping. For face-centered cubic (fcc) alloys, defects such as vacancies or edge dislocations were presumed to make a negligible contribution to reversible trapping, since the binding energy of H to such defects is considerably smaller than the activation energy for diffusion.¹⁴⁻¹⁶

The lattice diffusivity was determined by interpolation of data for a range of binary Cu-Ni alloys and was found to be $(3.0 \pm 0.1) \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ for 65Ni-35Cu at 25°C.¹⁷ The level of Cu differs slightly between the 65Ni-35Cu alloy and actual Alloy K-500 (30Cu), but the error in using the diffusivity of the 35Cu alloy for D_L was considered negligible. The apparent diffusivity for AA Alloy K-500 (assumed to be at ambient temperature) is $1.90 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$, which is only slightly higher than the value of $1.48 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ for the DA alloy.¹ These data were used to calculate values of k for the AA and DA alloys, as given in Table 3.

No data were available for the diffusivity for the annealed (unaged) alloy, so D_a was estimated from the values for the aged alloy. The intermetallic particles precipitated during aging appear to have little effect on D_a compared with that of the minor alloying elements in solid solution: D_a for the DA alloy was only about a factor of 2 smaller than D_L . Since most solutes introducing an electron vacancy provide reversible traps that could largely account for this factor, the intermetallics must be presumed to add little to the effect of the minor elements. Hence, it was assumed that D_a for the annealed alloy could be approximated to that for the AA alloy. By using this value and the D_L above, k was calculated for the annealed alloy (Table 3).

Susceptibility to HE

The irreversible trapping constants for the different heat treatments are presented graphically in Figure 1. It is clear that Alloy K-500 can exhibit a marked difference in irreversible trapping, depending on the type of heat treatment. Annealing caused a large increase in k for CD Alloy K-500 and thus can be considered to greatly heighten the intrinsic susceptibility (as represented by k) of this alloy. In fact, the values of k for all the 0.5-h-annealed specimens—

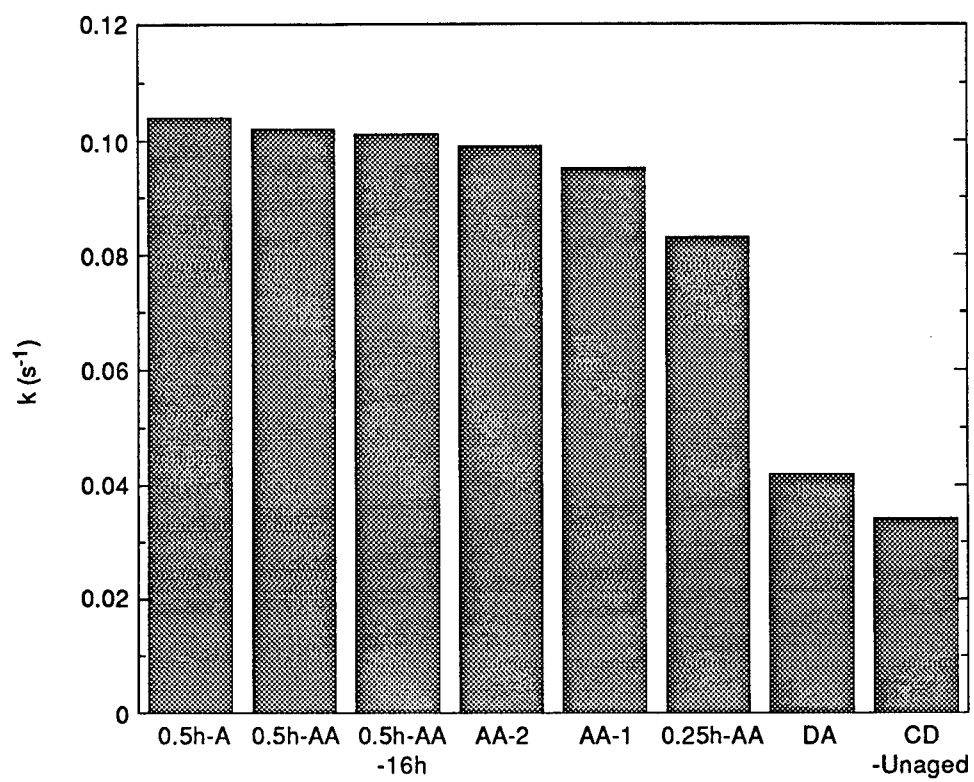


Figure 1. Variation in k for different heat treatments of Alloy K-500.

unaged or aged—were more than twice as large as that obtained for the direct aged CD specimen. Even halving the annealing time to 0.25 h resulted in a k double that of the DA alloy and only about 20% lower than the value obtained for the full (0.5-h) annealing time. Addition of the 0.5-h-annealing step before aging the CD alloy gave the same k values as those for the annealed and (16-h) aged alloy that was obtained elsewhere and tested previously.

The effect of 8-h aging on k was negligible for the annealed alloy and relatively small for the unannealed alloy. Doubling the aging time to 16 h for the annealed alloy did not affect k . Thus, the annealed alloy had similar values of k in the unaged and the aged (at least up to 16 h) conditions.

The results confirmed our postulate that the differences in irreversible trapping between the DA specimens and the earlier AA specimens resulted from differences in heat treatment. Moreover, they indicate that the key factor is the annealing step rather than the aging time and that annealing has quite a pronounced effect on the irreversible trapping characteristics of alloy K-500.

As noted above, tests on Alloy K-500 showed a difference in the ultimate tensile strength for DA and AA specimens cathodically precharged for 16 days.¹ The decrease (35%) in strength for the AA alloy coupled with the slight increase for the DA alloy indicated that the AA alloy is less resistant to HE than the DA alloy. The intrinsic susceptibilities for the two types of aged Alloy K-500 thus correlate with the observed resistances to HE, implying that the decrease in the resistance to HE produced by annealing is caused, at least in part, by changes in the irreversible traps.

Yield strength is a possible factor in the HE resistance of alloys and should be considered in the case of Alloy K-500, since it varied according to heat treatment. The yield strength was in the region of 700 MPa for the AA specimens but somewhat higher—1096 MPa—for the DA specimen. However, the AA specimens had higher values of k , which suggest that the difference in HE susceptibility between the specimens did not result from yield strength.

Identification of Irreversible Traps

In the previous work on Alloy K-500, the differences in thermomechanical processing were presumed to be responsible for differences in the species at grain boundaries. The principal irreversible trap in the DA alloy was thought to be grain boundary S for several reasons: (1) the intergranular HE of Ni¹⁸⁻²⁰ and Ni-Co alloys²¹ is assisted by S segregated at grain boundaries, and H also probably segregates to the grain boundaries as in Ni²⁰; (2) S has been identified as the critical segregant among three species (S, P, and Sb) in the intergranular HE of Ni because of its large enrichment at the grain boundaries¹⁹; (3) the calculated trap densities for two other high-Ni alloys, C-276 and UNS R30035, were in close agreement with the amount of grain boundary S

and P distributed per unit volume of the alloy¹³; (4) the sequence of the calculated trap densities for Alloy K-500 and a 77Cu-15Ni alloy was consistent with the levels of grain boundary segregants, based on the S-P contents of the alloys^{22*}; and (5) the small increase in k for Alloy K-500 with direct aging is consistent with a reduced volume diffusion of S thought to result from the addition of Cu to Ni.²³

The present results indicate that annealing considerably changes the number or the type of irreversible traps. Recent work by Natishan and coworkers has suggested that intergranular cracking of AA Alloy K-500 may be due to grain boundary C.^{5,6,24} The two AA heats used by these workers were the same as those in the present study. High-resolution scanning Auger electron spectroscopy showed graphitic C to be located on the intergranular facets and within grain boundaries.⁵ These two AA specimens differed from each other in heat treatment only with respect to annealing time yet exhibited levels of grain boundary C from 1-3% (AA-1) up to >20% (AA-2). Thus, annealing may render the alloy more prone to graphite precipitation. In the case of Ni 200, graphite has been observed at grain boundaries after prolonged exposure at temperatures between 425° and 650°C; that is, under typical aging conditions.^{3,4} However, the similarity in the values of k for the annealed/unaged and AA alloys suggests that graphite precipitation may actually initiate during annealing in the case of Alloy K-500. Alternatively, the increase in k with annealing (with or without aging) may reflect a change in some other microstructural feature and not, in fact, graphite precipitation.

Lee and Latanision found that the effect of S segregation on intergranular HE of Ni was most prominent when the grain boundaries were free of graphite precipitates.⁴ Accordingly, in the case of Alloy K-500, it is postulated that S governs HE of the DA alloy but C predominates in the AA alloy. If the respective critical segregants are S and C, k might be expected to be higher for the annealed alloy, since the total content of C is over 2 orders of magnitude greater than that of S. This rationale is in fact consistent with the actual results showing that k is higher for the annealed (aged or unaged) alloy than for the DA alloy, which does tend to support the assertion that k reflects graphite precipitation in the annealed alloy.

SUMMARY

- Irreversible trapping in CD Alloy K-500 can be strongly dependent on the type of heat treatment. Marked differences in k between DA and AA specimens can be attributed to the annealing step rather than to aging time.

* The intergranular concentration of S in Ni increases with total S content,²³ and it seems reasonable to expect similar behavior for Ni-Cu alloys.

- The intrinsic susceptibility to HE, as defined by k , is increased considerably by annealing, whereas aging has a negligible effect for the annealed alloy and only a modest effect for the unannealed alloy.
- The intrinsic susceptibilities for the AA and DA alloys can be correlated with the observed resistances to HE. Thus, the decrease in the resistance to HE produced by annealing appears to result to a large extent, if not entirely, from a change in the number or the type of irreversible traps.
- Differences in the species at grain boundaries in Ni and presumably in Ni-Cu alloys result from heat treatment, and these differences could account for changes in the type of irreversible traps. The higher k for the annealed (aged or unaged) alloy is consistent with the primary irreversible trap in this case being grain boundary graphitic C.

ACKNOWLEDGMENTS

Financial support of this work by the U.S. Office of Naval Research under Contract N00014-95-C-0313 is gratefully acknowledged.

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TABLE 1
Composition (wt%) of Cu-Containing Alloys

Element	K-500 DA	K-500 AA-1	K-500 AA-2
Al	2.92	2.95	2.95
C	0.16	<0.17	<0.14
Cu	29.99	29.53	29.8
Fe	0.64	<0.85	<0.74
Mn	0.72	<0.70	<0.58
Ni	64.96	65.29	65.1
P			<0.002
S	0.001	<0.001	<0.001
Si	0.15	<0.05	<0.15
Ti	0.46	0.46	0.44

TABLE 2
Values of k_a and J for Alloy K-500

Condition	Test	η (V)	E_c (V/SCE)	k_a (s ⁻¹)	J (nmol cm ⁻² s ⁻¹)	Mean k_a
0.5h-A	1	-0.30	-0.398	0.068	0.086	0.065 ± 0.002
		-0.35	-0.449	0.062	0.084	
		-0.40	-0.498	0.066	0.094	
	2	-0.30	-0.392	0.056	0.097	0.063 ± 0.005
		-0.35	-0.442	0.070	0.124	
		-0.40	-0.492	0.060	0.113	
		-0.45	-0.540	0.066	0.130	
	3	-0.30	-0.408	0.068	0.077	0.066 ± 0.001
		-0.35	-0.458	0.066	0.083	
		-0.40	-0.506	0.064	0.086	
0.5h-AA	1	-0.25	-0.351	0.063	0.062	0.064 ± 0.002
		-0.30	-0.399	0.065	0.071	
		-0.35	-0.448	0.062	0.078	
		-0.40	-0.496	0.063	0.085	
		-0.45	-0.544	0.068	0.093	
	2	-0.25	-0.351	0.059	0.068	0.064 ± 0.004
		-0.30	-0.400	0.070	0.091	
		-0.35	-0.448	0.061	0.088	
0.5h-AA-16h	1	-0.30	-0.394	0.060	0.078	0.061 ± 0.001
		-0.35	-0.445	0.060	0.080	
		-0.40	-0.495	0.062	0.084	
	2	-0.30	-0.407	0.063	0.064	0.066 ± 0.003
		-0.35	-0.456	0.064	0.077	
		-0.40	-0.504	0.070	0.085	
0.25h-AA	1	-0.25	-0.339	0.056	0.079	0.052 ± 0.004
		-0.30	-0.396	0.051	0.067	
		-0.35	-0.450	0.050	0.075	
		-0.40	-0.502	0.051	0.082	
		-0.45	-0.550	0.047	0.073	
		-0.50	-0.596	0.061	0.104	
		-0.55	-0.644	0.049	0.108	
	2	-0.25	-0.353	0.058	0.080	0.051 ± 0.004
		-0.30	-0.408	0.041	0.059	
		-0.35	-0.460	0.054	0.077	
		-0.40	-0.509	0.050	0.069	
		-0.45	-0.554	0.051	0.082	
		-0.50	-0.602	0.052	0.059	

TABLE 3
Trapping Constants for Alloy K-500

Condition	k_a (s ⁻¹)	D_L/D_a	k (s ⁻¹)
0.5h-A	0.065 ± 0.003	1.6	0.104 ± 0.008
0.5h-AA	0.064 ± 0.003	1.6	0.102 ± 0.008
0.5h-AA-16h	0.063 ± 0.003	1.6	0.101 ± 0.008
AA-2 (aged 16 h)	0.063 ± 0.003	1.6	0.099 ± 0.008
AA-1 (aged 16 h)	0.060 ± 0.006	1.6	0.095 ± 0.013
0.25h-AA	0.052 ± 0.004	1.6	0.083 ± 0.009
DA	0.021 ± 0.003	2.0	0.042 ± 0.007
CD-Unaged	0.017 ± 0.003	2.0	0.034 ± 0.007